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(21) International Application Number: PCT/US95/03564 (22) International Filing Date: 21 March 1995 (21.03.95) (30) Priority Data: 220,561 31 March 1994 (31.03.94) US (71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US). (72) Inventor: ONG, Shih-May, Christine; 26 Glenview Drive, Warren, NJ 07059 (US). (74) Agents: ROBERTS, Peter, W. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).			(81) Designated States: AU, CA, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: LLDPE RESIN BLENDS (57) Abstract A resin blend of LLDPE produced using a metallocene catalyst system and low density, high pressure polyethylene can be extruded into films exhibiting improved optical properties and impact strength.			

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LLDPE RESIN BLENDS

The invention relates to blends of linear low density copolymers of ethylene (LLDPE), and films thereof, which exhibit excellent optical properties.

5 Application of conventional linear low density polyethylene (LLDPE) in films which require excellent optical properties is limited because of inherent optical properties of the resin. The haze value of conventional LLDPE is generally greater than 10 [as measured by ASTM D-
10 1003].

Ethylene polymers which can be employed in applications requiring excellent optical properties are referred to as low density polyethylene (LDPE), which is produced at higher pressures than the pressure employed to
15 produce LLDPE. For example, LDPE is stated to be produced at 150-300 MPa [1500-3000 atm] at 200-300°C, while LLDPE is produced at 0.3-1.0 MPa [or 3 to 10 atmospheres] at 70-90°C (see KIRK-OTHMER, ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, Vol. 16, page 433 [Third Edition.]). However, LDPE resins
20 exhibit very low impact resistance.

Recently, new linear low density products have been produced with metallocene catalysts. This invention relates to the addition of high pressure PE resins and antiblocking agents, i.e. microtalc, to the new metallocene LLDPE resins
25 to achieve excellent optical properties with acceptable blocking characteristics. This invention is made possible because of the narrow molecular weight distribution and more uniform short chain branching distribution of the metallocene resin rather than the conventional LLDPE
30 resins.

The invention resides in a blend of 70 to 98 weight percent of an as-synthesized composition which is dry and solvent-free and comprises spherical, non-porous particles, which has an average particle size of 0.05 to 0.11 cm (0.02
35 to 0.045 inches), and a settled bulk density of 400 to 580 kg/m³ (25 to 36 lb/ft³), and which is a copolymer of ethylene and an alpha olefin, having a density of 0.902 to

0.929, a MFR of 15 to 25, and a M_w/M_n of 2.0 to 3.0; and 2 to 30 weight percent of low density polyethylene produced at 150-300 MPa [1500-3000 atm] and 200-300°C, wherein the haze value of the blend is less than 5 as measured by ASTM D-1003 and the dart drop impact resistance measured by ASTM D-1709 is greater than 400.

The LLDPE resin containing blends of the invention can be processed readily on commercial LLDPE film extruders without modifications. Films produced from the blends exhibit excellent impact properties which far exceed the impact properties of the LDPE.

The Low Density Polyethylene (LDPE) Component

The LDPE component employed in the blend of the invention is conventional and is produced at higher pressures than those employed to produce LLDPE. Thus the LDPE is produced at 150-300 MPa [1500-3000 atm] and 200-300°C, while LLDPE is typically produced at 0.3-1.0 MPa [or 3 to 10 atmospheres] and 70-100°C. Without the addition of the LLDPE component, the LDPE resin exhibits very low impact resistance.

Copolymer Component

The copolymer component of the blend of the invention is linear low density polyethylene (LLDPE) having a density of 0.902 to 0.929, most preferably ranging 0.915 to 0.922.

The LLDPE component of the blend of invention is different from conventional LLDPE in that it exhibits a haze value as measured by ASTM D-1003 of less than about 20, preferably from 3 to 10, most preferably from 5 to 7. By comparison, the haze value of conventional LLDPE is greater than 10.

The LLDPE component contains 0.1 to 2 ppm of Zr (from the catalyst used in its synthesis) and has an average particle size of 0.05 to 0.11 cm (0.02 to 0.045 inches), and a settled bulk density of 400 to 580 kg/m³ (25 to

36 lb/ft³). The as-synthesized resin is dry and solvent-free and comprises spherical, non-porous particles.

The LLDPE component of the invention blend exhibits a melt flow ratio (MFR) range of 15 to 25, preferably 15 to 20 and most preferably 16 to 18. MFR is the ratio I_{21}/I_2 [wherein I_{21} is measured at 190°C in accordance with ASTM D-1238, Condition F and I_2 is measured at 190°C in accordance with ASTM D-1238, Condition E.]

The LLDPE component exhibits an MI of 0.01 to 5, generally 0.1 to 5, and preferably 0.5 to 4, and most preferably 0.8 to 2.0. For blown film, the MI of the copolymer is preferably 0.5 to 1.5.

The melting point of the LLDPE component ranges from 95°C to 130°C. Furthermore, the hexane extractables content is very low, typically ranging from 0.3 to 1.0 wt.%. The M_w/M_n of the LLDPE component ranges from 2.0 to 3.0; M_w is the weight average molecular weight and M_n is the number average molecular weight, each of which is calculated from molecular weight distribution measured by GPC (gel permeation chromatography).

If the LLDPE component is processed into a film, without blending with LDPE in accordance with the invention, the film would exhibit balanced tear strength, as measured by ASTM D1922, ranging from 50 to 600, preferably from 220 to 420 for machine direction and from 200 to 700, preferably from 200 to 600 for the transverse direction. The film would also exhibit high modulus, as measured by ASTM D882 ranging from 7×10^4 to 48×10^4 kPa (1×10^4 to 6×10^4 psi), preferably from 15×10^4 to 31×10^4 kPa (2.2 to 4.5×10^4 psi) and high tensile yield, as measured by ASTM D882, ranging from 4800 to 21000 kPa (700 to 3000 psi), preferably from 12000 to 16000 kPa (1800 to 2300 psi).

If the LLDPE component is processed into a film, without blending with LDPE in accordance with the invention, the film would exhibit optical qualities as

determined by haze studies, measured by ASTM D-1003 between 3 and 20, preferably from 4 to 10. Films of inferior haze properties exhibit a haze of greater than 10. The importance of the optical properties of LLDPE depend on the intended application of the LLDPE resin. It is generally accepted that the poor optical properties of normal LLDPEs (haze >10 and gloss <50) severely limits their use in applications where optical performance is important.

The copolymer component of the resin blend of the invention is a copolymer of ethylene and one or more C_3 - C_{10} alpha-olefins, which preferably contains at least 80 weight % ethylene units. Suitable alpha olefins include propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, heptene-1 and octene-1. Preferably, the alpha-olefin comonomer is 1-butene, 1-hexene, and 1-octene. The most preferred alpha olefin is hexene-1. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/1-butene copolymers, ethylene/1-hexene copolymers, ethylene/4-methyl-1-pentene copolymers, ethylene/1-butene/1-hexene terpolymers, ethylene/propylene/1-hexene terpolymers and ethylene/propylene/1-butene terpolymers.

The LLDPE copolymer used in this invention is prepared from a new class of polyolefin catalyst comprising a carrier, an aluminoxane and at least one metallocene.

The catalyst carrier material is a solid, particulate, porous, inorganic or organic material, preferably inorganic material, such as an oxide of silicon and/or of aluminum. The carrier material is used in the form of a dry powder having an average particle size of 1 to 250 microns, preferably 10 to 150 microns. If necessary, the treated carrier material may be sieved to insure that the particles have an average particle size of preferably less than 150 microns. This is highly desirable in forming narrow molecular weight LLDPE, to reduce gels. The surface area

of the carrier is at least about 3 m²/gm, and preferably at least 50 m²/gm up to 350 m²/gm. When the carrier is silica, it is preferably heated to 100°C to 850°C and most preferably at about 250°C. The carrier material used to
5 produce the catalyst composition should have at least some active hydroxyl (OH) groups.

In the most preferred embodiment, the carrier is silica which, prior to the use thereof, is dehydrated by fluidizing it with nitrogen and heating at about 250°C for
10 about 4 hours to achieve a surface hydroxyl group concentration of about 1.8 millimoles per gram (mmols/gm). The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area = 300 m²/gm; pore volume of 1.65 cm³/gm) marketed under the tradenames
15 of Davison 952-1836, Davison 952 or Davison 955 by the Davison Chemical Division of W.R. Grace and Company. The silica is in the form of spherical particles, e.g., as obtained by a spray-drying process.

The aluminoxane used in the LLDPE catalyst composition
20 comprises oligomeric linear and/or cyclic alkylaluminoxanes represented by the formula:

$R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear aluminoxanes and
 $(-Al(R)-O)_m$ for oligomeric cyclic aluminoxane wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is
25 a C₁-C₈ alkyl group and preferably methyl. Methylalumin-oxane (MAO) is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 1000. MAO is typically kept in solution in toluene.

30 The metallocene compound has the formula $Cp_mMA_nB_p$ in which Cp is an unsubstituted or substituted cyclopentadienyl group, M is a transition metal selected from zirconium or hafnium and A and B belong to the group including a halogen atom, hydrogen or an alkyl group. In
35 the above formula of the metallocene compound, the preferred transition metal atom M is zirconium. In the

above formula of the metallocene compound, the Cp group is an unsubstituted, a mono- or a polysubstituted cyclopentadienyl group. The substituents on the cyclopentadienyl group can be preferably straight-chain or branched C_1-C_6 alkyl groups. The cyclopentadienyl group can be also a part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when m in the above formula of the metallocene compound is equal to 2, the cyclopentadienyl groups can be also bridged by polymethylene or dialkylsilane groups, such as $-CH_2-$, $-CH_2-CH_2-$, $-CR'R''-$ and $-CR'R''-CR'R''-$ where R' and R'' are short alkyl groups or hydrogen, $-Si(CH_3)_2-$, $Si(CH_3)_2-CH_2-CH_2-Si(CH_3)_2-$ and similar bridge groups. If the A and B substituents in the above formula of the metallocene compound are halogen atoms, they belong to the group of fluorine, chlorine, bromine or iodine. If the substituents A and B in the above formula of the metallocene compound are alkyl or aromatic groups, they are preferably straight-chain or branched C_1-C_8 alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl.

Suitable metallocene compounds include bis(cyclopentadienyl)metal dihalides, bis(cyclopentadienyl)metal hydridohalides, bis(cyclopentadienyl)metal monoalkyl monohalides, bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal dihalides wherein the metal is titanium, zirconium or hafnium, halide groups are preferably chlorine and the alkyl groups are C_1-C_6 alkyls. Illustrative, but non-limiting examples of metallocenes include bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)-hafnium dichloride, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium hydridochloride, bis(cyclopentadienyl)hafnium hydridochloride,

bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(isobutylcyclopentadienyl) zirconium dichloride, cyclopenta-dienyl-
5 zirconium trichloride, bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)] zirconium dichloride.

The mole ratio of aluminoxane provided aluminum, expressed as Al, to metallocene metal expressed as M (e.g. Zr), ranges from 50 to 500, preferably 75 to 300, and most preferably 100 to 200. An added advantage of the present invention is that this Al:Zr ratio can be directly controlled. In a preferred embodiment the aluminoxane and
15 metallocene compound are mixed together in a suitable co-solvent at a temperature of 20 to 80°C, for 0.1 to 6.0 hours, prior to reaction with the carrier. The co-solvent for the metallocene and aluminoxane can be aromatic hydrocarbons, halogenated hydrocarbon or halogenated
20 aromatic hydrocarbons, preferably toluene.

A particularly desirable method for producing linear low density polyethylene polymers is in a single fluid bed reactor such as that described in U.S. Patent No. 4,481,301. The process conditions would include a
25 temperature below the sintering temperature of the polymer particles, preferably 60° to 115°C, and more preferably 75° to 95°C, and a pressure of 150 to 350 psig (1100 to 2500 kPa).

A "diluent" gas nonreactive under the conditions in
30 the polymerization reactor, such as nitrogen, argon, helium, methane, or ethane, is preferably present during the copolymerization of the LLDPE. Hydrogen can also be present as a chain transfer agent.

The Invention Blends

The blends of the invention comprise 70 to 98, preferably 90 to 98, and most preferably 95 to 98 weight percent of the LLDPE copolymers described above and 2 to 30, preferably 2 to 10, and most preferably 2 to 5 weight percent of conventional LDPE resin.

The blends products may also contain any of various additives conventionally added to polymer compositions such as lubricants, microtalc, stabilizer, antioxidants, compatibilizers, pigments, etc. These additives can be employed to stabilize the products against oxidation. For example, additive packages comprising 400-1200 ppm hindered phenol(s); 700-2000 ppm phosphites; 250 to 1000 ppm antistats and 250-1000 ppm stearates, for addition to the resin powders, can be used for pelletization.

The polymer blend can be added directly to a blown film extruder, e.g., a Sterling extruder, to produce films having a thickness, for example of 0.5 to 5 mils (0.013 to 0.13 mm).

Films produced from the blend of the invention have improved optical properties (haze <5 and gloss >70). Films produced from the invention blend also exhibit Dart Drop Impact values as measured by ASTM D-1709 greater than 400, generally from 500 to 1500.

The following Examples further illustrate the essential features of the invention.

The properties of the polymers produced in the Examples were determined by the following test methods:

Density	ASTM D-1505 - a plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity. Measurement for density is then made in a density gradient column; reported as gms/cc.
Melt Index (MI), I ₂	ASTM D-1238 - Condition E Measured at 190°C - reported as grams per 10 minutes.

High Load ASTM D-1238 - Condition F
Melt Index Measured at 10.5 times the weight used in
(HLMI), I_{21} the melt index test above.

5 Melt Flow I_{21}
Ratio (MFR) I_2

Example 1

10 A 1 I_2 , 0.918 density pilot plant LLDPE metallocene
resin produced in accordance with Example A, below, was
compounded on a Banbury mixer using 1000 ppm Irganox 1010,
2000 ppm Irgafos 168, 1000 ppm Erucamide, 5000 ppm ABT
2500, 500 ppm AS990 and 500 ppm ZnSt. The pelletized
metallocene resin was then blended with a commercial high
pressure ethylene low density resin (Mobil LBA-133) of 2
15 I_2 , 0.924 density at three different levels -0%, 5% and
10%. A 1 mil (0.03 mm) film was then produced from each
blend using a 2.5 inch (6.4 cm) Brampton blown film
extruder at 440°C, 100 mil (2.5 mm) die gap, and a resin
feed of 150 lbs/hr (68 kg/hr). A broader molecular weight
20 distribution commercial LLDPE resin, Mobil NTX-095, was
also blended at with LBA-133 two levels, for comparison
purposes. These results were then compared with a 1 mil
film made from Rexene 1065 (1.9 I_2 , 0.924 density), a
commercial high clarity LDPE resin.

25 The results (see Table I) show that at the 5% LLDPE
blend level, the metallocene/LDPE blend gave comparable
haze to that of Rexene 1065 (4.4 vs. 4.6 for Rexene) while
offering superior impact properties (i.e. dart impact of
750 vs 64 gms for Rexene 1065). Furthermore, at the same
30 LDPE blend level, impact properties of the metallocene/LDPE
blend were superior to those of NTX-095/LDPE blend. The
metallocene blend offered lower haze (4.4% vs 10.3% for
NTX-095 blend) and superior dart impact property (750 gms
vs 166 gms for the NTX-095 blend).

Table I**High Clarity Metallocene Blend Study**

	Base Resin	% LDPE	% Haze	DDI, gms
5	Metallocene Produced Resin(a)	5	4.4	750
	Metallocene Produced Resin(a)	0	7.0	>800
	NTX-095	5	10.0	166
	NTX-095	0	17.0	264
10	Rexene 1065(b)	0	4.6	64

(a) Produced as in Example A.

(b) Rexene 1065 was run on the Brampton film extruder at 360°C and 40 mil (1 mm) die gap, with other conditions being the same.

15

Example A

Raw materials used in catalyst preparation included 504 g of Davison 952-1836 silica, 677 g of methylaluminumoxane in toluene solution (30 wt.% MAO), 7.136 g of bis(n-butylcyclopentadienyl)zirconium dichloride.

20

The steps of the catalyst preparation are set forth below:

1. Dehydrate the 952-1836 silica at 250°C for 4 hours using air to purge. Then purge with nitrogen on cooling.
- 25 2. Transfer the silica to a mix-vessel.
3. Add 7.136 g of bis(n-butylcyclopentadienyl) zirconium dichloride and 677 g of methylaluminumoxane to a bottle.
4. Agitate the catalyst solution in the bottle until the metallocene dissolves in the MAO solution.
- 30 5. Transfer the MAO and metallocene solution into the mix-vessel containing the dehydrated 955 silica slowly while agitating the silica bed vigorously to make sure that the catalyst solution is well dispersed into the silica bed.
- 35

6. After the addition, continue to agitate the catalyst for 1/2 hours.
 7. Start drying the catalyst by purging with nitrogen for 5 hours at 45°C.
 - 5 8. Sieve the catalyst to remove particles larger than 150 micron.
 9. The catalyst has the following analysis:
Yield = 767 g catalyst (from 500 g of silica)
Al = 9.95 wt.%
10 Zr = 0.19 wt.%
- LLDPE resin was produced from the above catalyst in a fluid bed gas phase reactor using the following process conditions:

Process Conditions:

15	Fluidization velocity	1.7 ft/sec (0.5 m/sec)
	Residence time	2.5 hours
	Temperature	84 °C
	Ethylene	220 psi
	Hexene	3.6 psi
20	Isopentane	50 psi
	Carbon dioxide	3 ppm
	Ash	200-300 ppm
	The resulting resin had the following characteristics:	
	I ₂	1
25	density	0.918
	Mw/Mn	2.6
	MFR	18
	Melting point	115°C

CLAIMS:

1. A blend comprising 70 to 98 weight percent of an as-synthesized composition which is dry and solvent-free and comprises spherical, non-porous particles, which
5 has an average particle size of 0.05 to 0.11 cm (0.02 to 0.045 inches), and a settled bulk density of 400 to 580 kg/m³ (25 to 36 lb/ft³), and which is a copolymer of ethylene and an alpha olefin, having a density of 0.902 to 0.929, a MFR of 15 to 25, and a M_w/M_n of 2.0
10 to 3.0; and 2 to 30 weight percent of low density polyethylene produced at 150-300 MPa [1500-3000 atm] and 200-300°C, wherein the haze value of the blend is less than 5 as measured by ASTM D-1003 and the dart drop impact resistance measured by ASTM D-1709 is
15 greater than 400.
2. The blend of Claim 1, wherein said alpha olefin of said copolymer has 3 to 10 carbon atoms.
3. The blend of Claim 1, wherein the alpha olefin
20 selected from butene, hexene, octene and admixtures thereof.
4. The blend of any preceding claim comprising 90-98 weight% of said copolymer and 2-10 weight% of said low density polyethylene.
5. The blend of any preceding claim comprising 95-98
25 weight% of said copolymer and 2-5 weight% of said low density polyethylene.
6. A film formed from the blend as claimed in any preceding claim.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/03564

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C08L 23/06, 23/08, 23/16, 23/20 US CL : 525/240 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 525/240 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,243,619 (FRASER ET AL) 06 June 1981. See columns 2, 4, 7, 17, 19, 27 and 29-32.	1-4
Y	US, A, 4,587,303 (TURTLE) 06 May 1986. See columns 2, 3 and 5.	1-4
Y	US, A, 4,833,111 (NOWLIN) 23 May 1989. See columns 1-3, 9 and 10.	1-4
Y	WO, A, WO 90/03414 (EXXON CHEMICAL PATENTS INC.) 05 April 1990. See pages 3, 6-8 and 11-18.	1-4
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 31 MAY 1995		Date of mailing of the international search report 17 JUL 1995
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer <i>Gene Weaver for</i> CARMAN SECCURO Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/03564

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5 & 6
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.